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Transition Metal Complexes as Potential Semiconductors
by

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Introduction

Transition metal complexes present interesting possibilities for the elucidation of the factors influencing the electrical conductivities of solids. This research is directed toward a better understanding of the process of electron transport in solids through studies of electrical properties of a series of related complexes.

Consider the work of Verwey and Haayman¹ on spinels, e.g. Fe_3O_4 , Fe_2AlO_4 , Mn_3O_4 . They find that Fe_3O_4 , an inverted spinel, has low resistivity relative to Fe_2AlO_4 and Mn_3O_4 , both normal spinels. They ascribe the conductivity to the process $\text{Fe}^{+2}-\text{O}-\text{Fe}^{+3} \longrightarrow \text{Fe}^{+3}-\text{O}-\text{Fe}^{+2}$ and argue that the low resistivity of Fe_3O_4 derives from the circumstance that in the inverted spinel there are oxygen-bridged Fe^{+2} and Fe^{+3} ions both in octahedral holes; the normal spinels place the +2 ions in tetrahedral holes and the +3 ions in octahedral holes. Apparently one factor influencing conductivity is the availability or lack thereof of several sites of equal energy between which the conduction electrons can move.

In discussing $\text{Li}_x\text{Ni}_{1-x}\text{O}$, Mott² points out a similar energetic restriction, noting that as the lattice parameter approaches infinity, the minimum value for the activation energy for electron transport must be no less than the difference between the ionization potential of the electron donor and the electron affinity of the electron acceptor. The very different electrical properties of NiO itself, a very poor conductor, and $\text{Li}_x\text{Ni}_{1-x}\text{O}$, of low resistivity,

may then be rationalized: in the former, the charge transfer process may be represented by the endothermic $\text{Ni}^{+2}-\text{O}-\text{Ni}^{+2} \longrightarrow \text{Ni}^{+1}-\text{O}-\text{Ni}^{+3}$, while in the latter, the resonant process $\text{Ni}^{+2}-\text{O}-\text{Ni}^{+3} \longrightarrow \text{Ni}^{+3}-\text{O}-\text{Ni}^{+2}$ may be invoked.

Heikes and Johnston³ ascribe the activation energy for electron transfer in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ to local strains in the lattice caused by the charge transfer. It is therefore of interest to investigate systems wherein bond lengths are relatively insensitive to oxidation state, in order to minimize such local strains.

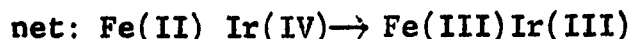
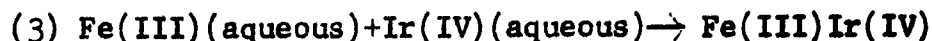
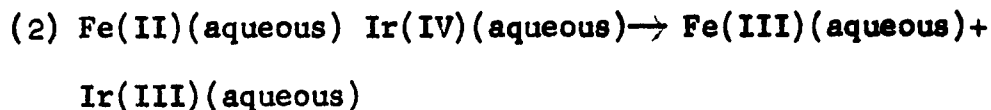
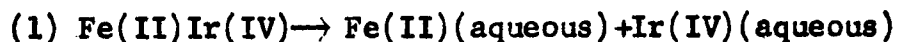
In the realm of solution chemistry, a distinction may be drawn between reactions proceeding through a bridged activated complex, of which the above systems are solid state analogs, and reactions wherein the coordination spheres of the reactants remain distinct. The bridged activated complex apparently derives its efficiency in solution from stabilization of the activated complex by bridge formation; since, in the solid state, there can be no such factor, bridges being either always or never present, and since bridged systems might be expected to maximize strains, it is of interest to study systems which are the solid state analogs of the outer sphere activated complex in solution.

Morin⁴ has found that it is possible to correlate the electrical properties of solid metal oxides with the overlap integrals $S(t_{2g}, t_{2g})$ and $S(t_{2g}, p\pi)$, where t_{2g} is a metal orbital transforming like t_{2g} under O_h and $p\pi$ is an oxygen π orbital. He finds that, if

either overlap integral is large, metallic behavior is found. One interpretation that may be placed on this result is this: that either direct metal-metal interaction, or oxygen-mediated interaction can serve to mobilize electrons. It is the direct metal-metal interaction that one invokes in the outer sphere activated complex.

Choice of System

Consider the compound $\text{Fe}(\text{phen})_3\text{IrCl}_6$, (phen = 1,10-phenanthroline), typical of those which we are studying. This compound has two possible formulae, Fe(II)Ir(IV) and Fe(III)Ir(III) in an obvious notation. As all ions are low-spin, transformation of the one into the other may be represented by $\text{Fe}(t_{2g}^6)\text{Ir}(t_{2g}^5) \rightarrow \text{Fe}(t_{2g}^5)\text{Ir}(t_{2g}^6)$, regarding both complexes as octahedral. As charge transfer involves only t_{2g} electrons, and the t_{2g} electrons are delocalized over the ligands, bond lengths should be relatively insensitive to oxidation state, and lattice strains and bond stretching prior to electron transfer should be relatively small. Energetically, consideration of the cycle



leads to $\Delta F_{\text{net}}^0 = -RT \ln K_{\text{sp}}^1 + \Delta E^0 + RT \ln K_{\text{sp}}^3$, which will be seen to be small; thus, in this compound there are two sites, Fe(III) and

Ir(IV), of roughly equal energy accessible to the "last" electron. Moreover, in solution, redox reactions between ions such as these are known to be rapid⁵, and it is the entropy of activation, which may be related to the barrier penetration probability of the electron, which makes them so. It is on the basis of such considerations as these that we have chosen our systems; we hope to gain insight in the solid state problem by application of some of the things which we know from solution chemistry, recognizing that such things as exciton interactions, order-disorder phenomena, etc. may arise. By systematic variation of our systems, both in regard to the central atoms and to the ligands, we hope to see how far the analogy between solution chemistry and solid state chemistry extends.

Experimental Techniques

All compounds have been prepared by standard methods requiring no comment.

As single crystals of appreciable size are very difficult to obtain, measurements are performed on pressed pellets, the surfaces of which to which contact is made being painted with DuPont Silver 4545. Samples are placed in an oven which also serves as electrical shield, and resistances are measured with a General Radio Model 1230A D.C. Amplifier and Electrometer. Initially, a Heathkit VTVM was used for survey purposes; it was calibrated against precision resistors up to 10^8 ohm, but did not afford us sufficient range. Physical dimensions of pellets are obtained with a micrometer.

Results

$\text{Fe}^{\text{II}}(\text{phen})_3\text{Ir}^{\text{IV}}\text{Cl}_6$, prepared from $\text{Fe}^{\text{II}}(\text{phen})_3\text{Cl}_2$ and $\text{Na}_2\text{Ir}^{\text{IV}}\text{Cl}_6$, is a maroon material with a magnetic susceptibility which, when corrected for diamagnetism, corresponds to one unpaired electron, as might be expected; our magnetic measurements are not sufficiently precise to detect any small temperature-independent paramagnetism characteristic of a metal. $\text{Fe}^{\text{III}}(\text{phen})_3\text{Ir}^{\text{III}}\text{Cl}_6$, prepared from $\text{Fe}(\text{phen})_3\text{Cl}_3$ and Na_3IrCl_6 , is a blue-green material which upon standing changes to a maroon color, i.e. to $\text{Fe}^{\text{II}}(\text{phen})_3\text{Ir}^{\text{IV}}\text{Cl}_6$. From the electrical conductivity of saturated solutions of $\text{Fe}^{\text{II}}(\text{phen})_3\text{Ir}^{\text{IV}}\text{Cl}_6$ and of $\text{Co}^{\text{III}}(\text{phen})_3\text{Ir}^{\text{III}}\text{Cl}_6$ (assumed to have the same solubility as $\text{Fe}^{\text{III}}(\text{phen})_3\text{Ir}^{\text{III}}\text{Cl}_6$) and the standard electrode potentials of the $\text{Fe}(\text{II})$ - $\text{Fe}(\text{III})$ and $\text{Ir}(\text{III})$ - $\text{Ir}(\text{IV})$ couples, -1.06 v.^6 and -1.02 v.^7 respectively, we estimate that ΔF for the process $\text{Fe}(\text{II})\text{Ir}(\text{IV}) \rightarrow \text{Fe}(\text{III})\text{Ir}(\text{III})$ is 0^+3 k-cal , a number which we are now refining; indeed, the observation that $\text{Fe}(\text{II})\text{Ir}(\text{IV})$ spontaneously changes to $\text{Fe}(\text{II})\text{Ir}(\text{IV})$ allows us to discard negative values of ΔF^0 .

We find no spectral anomalies in $\text{Fe}^{\text{II}}(\text{phen})_3\text{Ir}^{\text{IV}}\text{Cl}_6$ in the range $400 \text{ m}\mu$ to 8μ ; in this range the spectrum can be represented as the sum of the spectra of the components as chloride and as sodium salt respectively. We find no electron spin resonance signal at room temperature, unfortunately the only temperature presently accessible on the apparatus available to us. Measurement of conductivity have been as yet limited to the observation that, according

to the VTVM, the conductivity is less than $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Our acquisition of the General Radio Electrometer has enabled us to initiate conductivity studies which are both more precise and more reliable. Thus far, measurements are restricted to the following systems: alkali-free Prussian blue, a run to test our methodology, the nitrosylpentacyanoferrate analog of Prussian blue, a material of substantially lower conductance than Prussian blue itself in accord with our premise that redox potentials in solution can relate to conductances of solids; $\text{Fe}^{\text{II}}(\text{GBNMI})_3\text{Ir}^{\text{IV}}\text{Cl}_6$ (GBNMI = glyoxalbis-N-methylimine) a ligand giving complexes very similar to phen^8 , but sterically much less demanding); $\text{Fe}^{\text{II}}(\text{GBNMI})_3\text{Pt}^{\text{IV}}\text{Cl}_6$; $\text{Fe}^{\text{II}}(\text{GBNMI})_3\text{Sn}^{\text{IV}}\text{Cl}_6$. The conductivity of the $\text{IrCl}_6^=$ compound can be adequately described by $\tau = 2 \times 10^{-3} e^{-0.56 \text{ eV}/kT}$; for the $\text{SnCl}_6^=$ compound, $\tau = 10^9 e^{-1.6/kT}$. The surprisingly large preexponential factor is being reinvestigated. Thus far, plots of $\ln \tau$ vs $1/T$ for the $\text{P}+\text{Cl}_6^=$ compound show curvature, the origin of which (or even reality of which) is to date unknown.

Footnotes

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